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Table 1. Calculated Total Energies (E_{tot}, hartrees) of Semibullvalene in C_s (**1**) and C_{2v} (**2**)

Level	E_{tot} (**1**)	E_{tot} (**2**)
HF/3-21G	-305.79896	-305. 77767
HF/6-31G*	-307.51196	-307.48324
MP2(fu)/6-31G*	-308.57882	-308.57052
Becke3LYP/6-31G*	-309.57481	-309.56587
Becke3LYP/6-311G* [a]	-309.63799	-309.62970
Becke3LYP/6-311+G* [a]	-309.64100	-309.63327
Becke3LYP/6-311+G(2d,p) [a]	-309.66170	-309.65466
(6,6)CASSCF/3-21G	-305.86588	-305.86588
(6,6)CASSCF/6-31G* [b]	-307.58536	-307.56872
CASPT2N/6-31G* [b]	-308.57757	-308.56478
(6,6)CASSCF/6-31G*	-307.58678	-307.56969
CASPT2N/6-31G* [c]	-308.57903	-308.56424
CASPT2N/6-31G* [d]	e	-308.56776

a) Using Becke3LYP/6-31G* geometries. b) Using (6,6)CASSCF/3-21G geometries. c) Using (6,6)CASSCF/6-31G* geometries. d) Minimum energy geometry predicted using three CASPT2N energies fitted to a quadratic equation (see text). e) Not calculated for C_s structure; and the CASPT2N/6-31G*//(6,6)CASSCF/6-31G* C_s energy was used for the E_{rel} calculation.

Table 2. Calculated Total Energies (E_{tot}, hartrees) of 1,5-Methanosemibullvalene in C_s (**3a**) and C_{2v} (**3**).

Level	E_{tot} (**3a**)	E_{tot} (**3**)
HF/6-31G*	-345.29350	-345.27435
Becke3LYP/6-31G*	-347.60000 [d]	-347.60584
(6,6)/CASSCF/3-21G	-343.43623	-343.45258
(6,6)/CASSCF/6-31G* [a]	-345.36832	-345.38121
CASPT2N/6-31G* [a]	-346.49858	-346.50547
(6,6)/CASSCF/6-31G*	-345.37056	-345.38188
(6,6)/CASSCF/6-311G** [b]	-345.45166	-345.46346
CASPT2N/6-31G* [b]	-346.50062	-346.50584
CASPT2N/6-31G* [c]	e	-346.50678

a) Using (6,6)CASSCF/3-21G geometries. b) Using (6,6)CASSCF/6-31G* geometries. c) Minimum energy geometry predicted using three CASPT2N energies fitted to a quadratic equation (see text). d) Becke3LYP/6-31G* single-point using the HF/6-31G* geometry, since C_s form collapses to the C_{2v} form at Becke3LYP/6-31G*. e) Not calculated for C_s structure; and the CASPT2N/6-31G*//(6,6)CASSCF/6-31G* C_s energy was used for the E_{rel} calculation.

Table 3. Calculated Total Energies (E_{tot}, hartrees) of 2,8:4,6-Bisethanosemibullvalene in C_s (**4a**) and C_{2v} (**4**).

Level	E_{tot} (**4a**)	E_{tot} (**4**)
HF/3-21G	-458.69544	-458.69350
HF/6-31G*	-461.26623	-461.26092
MP2(fc)/6-31G*	-462.82387 [a]	-462.83834
Becke3LYP/6-31G*	-464.36916[a]	-464.38046
(6,6)CASSCF/3-21G	b	-458.78987
(6,6)CASSCF/6-31G*	-461.34435	-461.35019
CASPT2N/6-31G* [c]	-462.88497	462.89179
CASPT2N/6-31G* [d]	e	-462.89436

a) Using the C_s symmetric HF/6-31G* geometry for single-point energy calculations, since C_s form does not exist at MP2 and Becke3LYP. b) The RHF/3-21G optimized C_s geometry collapsed to the C_{2v} structure upon attempted optimization at the (6,6)CASSCF/3-21G level. c) Using the CASSCF(6,6)/6-31G* geometry. d) Minimum energy geometry predicted using three CASPT2N energies fitted to a quadratic equation (see text). e) Not calculated for C_s structure; and the CASPT2N/6-31G*//(6,6)CASSCF/6-31G* C_s energy was used for the E_{rel} calculation.

Table 4. Calculated Total Energies (E_{tot}, hartrees) for strained semibullvalenes **5-7**.

	HF/6-31G*	MP2(fc)/6-31G*	Becke3LYP/6-31G*
5	-383.10608	-384.42936	-385.67417
5-Li$^+$			-393.00373
6a	-345.31727	-346.48754	-347.62943
7a	-384.38571	-385.68316	-386.97268 [a]
7b	-384.39104	-385.68578	-386.97596 [a]

a) The zero-point energies are 105.9 kcal/mol for **7a** and 106.9 kcal/mol for **7b**.

Table 5. (6,6)CASSCF/6-31G* and CASPT2N/6-31G* Total Energies (E_{tot}, hartrees) of Semibullvalene , Methanosemibullvalene, and Bis(ethano)semibullvalene

Compound	E_{tot}	
$^1A_1$ Excited State	CASSCF	CASPT2N
1 (C_s)		
$1(^1A') \rightarrow 1(^1A'')$	-308.35885	
$1(^1A') \rightarrow 2(^1A')$	-308.35237	
3a (C_s)		
$1(^1A') \rightarrow 1(^1A'')$	-346.30144	
$1(^1A') \rightarrow 2(^1A')$	-346.29676	
2 (C_{2v})		
$1(^1A_1) \rightarrow 1(^1B_1)$	-308.42849	-308.40725
$1(^1A_1) \rightarrow 1(^1B_2)$	-308.44235	-308.42085
$1(^1A_1) \rightarrow 1(^1A_2)$	-308.39883	-308.35901
$1(^1A_1) \rightarrow 2(^1A_1)$	-308.38942	-308.29863
3 (C_{2v})		
$1(^1A_1) \rightarrow 1(^1B_1)$	-346.38883	-346.38589
$1(^1A_1) \rightarrow 1(^1B_2)$	-346.43400	-346.42102
$1(^1A_1) \rightarrow 1(^1A_2)$	-346.39088	-346.37747
$1(^1A_1) \rightarrow 2(^1A_1)$	-346.41755	-346.38789
4 (C_{2v})		
$1(^1A_1) \rightarrow 1(^1B_1)$	-462.76819	-462.76276
$1(^1A_1) \rightarrow 1(^1B_2)$	-462.79845	-462.78268
$1(^1A_1) \rightarrow 1(^1A_2)$	-462.74428	-462.72566
$1(^1A_1) \rightarrow 2(^1A_1)$	-462.67735	-462.65954